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【書類名】 明細書

【発明の名称】 マルチフィラメント及びその製造方法

【特許請求の範囲】

【請求項1】 L体が98%以上であり、相対粘度が2.7～3.9であり、モノマー量が0.5重量%以下であり、Sn（錫）の含有量が30ppm以下であり、直鎖状であるポリ乳酸樹脂からなる事を特徴とするマルチフィラメント。

【請求項2】 L体が98%以上であり、モノマー量が0.5重量%以下であり、Sn（錫）の含有量が30ppm以下であり、直鎖状であり、分子量が重量平均分子量Mw：12万～22万、数平均分子量Mn：6万～11万である事を特徴とするマルチフィラメント。

【請求項3】 引張強度4.5g/d以上、沸水収縮率が12%以下で、複屈折が0.030以上、熱応力のピーク温度が85℃以上である請求項1又は2記載のマルチフィラメント。

【請求項4】 ポリ乳酸繊維を製造するに際して、請求項1又は2に記載のポリ乳酸を用い、3000m/分以上4500m/分以下で紡糸した後、延伸温度100℃～125℃で、1.3倍以上延伸した後、125℃～150℃で熱セットする事を特徴とするポリ乳酸マルチフィラメントの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】

本発明は、生分解性を有する合成繊維並びに当該繊維の製造方法に関する。

【0002】

【従来の技術】

現在最も広く利用されているマルチフィラメント繊維素材は、ポリエチレンテレフタレートに代表されるポリエステルや、6ナイロン、66ナイロンに代表されるポリアミドなどの合成樹脂である。

【0003】

合成樹脂は大量に安価に製造できるというメリットがある反面、使用後の廃棄

方法をめぐる問題がある。すなわち、上述した合成樹脂からなる繊維は自然環境中では殆ど分解せず、焼却をすると高い燃焼熱を発生する恐れがある。

【0004】

そこで、最近では生分解性を有する合成樹脂であるポリカプロラクトンやポリ乳酸等を繊維用途に利用する提案がなされている。確かにこれらの合成樹脂は生分解性を有するという長所があるが、従来の（非生分解性）合成樹脂に較べて実用性という点では問題が多い。

【0005】

従来ポリ乳酸系生分解性繊維は、3000m/分以下の低速で紡糸した後、延伸行程を行うコンベンショナル法で繊維を製造する方法が採用されている。例えば、特開平7-216646号公報や、特開平7-133569号公報では、1000m/分以下で紡出した未延伸ポリ乳酸繊維を巻き取り、延伸行程にて配向繊維を得る方法が提案されているがポリエチレングリコールを共重合する必要がある。

【0006】

しかし、これらの方法でも、製造工程の操業性を改良する事は難しく、従来の（非生分解性）合成樹脂を原料とする繊維に匹敵する物性・操業性の繊維を得ることはできなかった。

【0007】

【発明が解決しようとする課題】

本発明者等は、繊維の原料となるポリ乳酸の物性を厳しく吟味し、特定の物性のポリ乳酸を用い、紡糸・延伸工程を検討する事によって、強度、伸度、沸収等の物性値がポリエステル、ナイロン繊維並みの物性を有し、織り・編み・染色等の後工程でも、ポリエステル、ナイロン繊維並みの加工性を得る事のできるポリ乳酸マルチフィラメントの製造方法を提供するにある。

【0008】

【課題を解決する為の手段】

上述の目的は、L体が98%以上であり、相対粘度が2.7～3.9であり、モノマー量が0.5重量%以下であり、Sn（錫）の含有量が30ppm以下で

あり、直鎖状であるポリ乳酸樹脂からなる事を特徴とするマルチフィラメントにより達成できる。。

【0009】

【発明の実施の形態】

本発明に用いるポリ乳酸は直鎖状の構造を有する。すなわち分岐構造を殆ど持たないものである。従来提案では、熔融粘度や重合度を改良する目的でポリ乳酸を重合する際に少量の分岐剤を添加する事が行われていた。しかしながら、ポリ乳酸繊維の製造に際しては、原料樹脂の分岐構造は、通常のポリエステル繊維に比べて、はるかに紡糸操業性にマイナスに作用する事が本発明者等によって確認された。すなわち分岐構造が僅かでも存在するポリ乳酸は分岐構造が無い物に比べると引っ張り強度が弱いという問題がある。

【0010】

分岐構造を排する為には、ポリマーの原料に分岐構造を生成させるもの、3価、4価のアルコールやカルボン酸等を一切利用しないのが良いが、何らかの別の理由でこれらの構造を持つ成分を使用する場合であっても、紡糸時の糸切れ等、紡糸操業性に影響を及ぼさない必要最小限度の量にとどめることが肝要である。

【0011】

本発明に用いるポリ乳酸はL-乳酸とD-乳酸、あるいは乳酸の2量体であるL-ラクチドやD-ラクチドを原料とするものであるが、L-体の比率が98%以上のものであることが肝要である。これはD-体の比率が上昇すると非晶構造になり、紡糸・延伸工程で配向結晶が進まず、得られる繊維の物性が劣る為である。特に引っ張り強度が著しく低下し、一方沸水収縮率が過大となり、実用上使用する事が不可能である。

【0012】

本発明に用いるポリ乳酸は、ポリマー中のSnの含有量が30ppm以下である必要があり、好ましくは20ppm以下である。Sn系の触媒はポリ乳酸の重合触媒として使用されるが、30ppmを超える量存在すると、紡糸時に解重合が起きてしまい、口金濾過圧が短時間で上昇し、紡糸操業性が著しく低下する。

【0013】

S n の量を少なくする為には、重合時に使用する量を少なくしたり、チップを適当な液体で洗浄すればよい。

【 0 0 1 4 】

本発明に用いるポリ乳酸は、モノマーの含有量が 0 . 5 重量%以下、好ましくは 0 . 3 重量%以下、特に好ましくは 0 . 2 重量%以下である。本発明に言うモノマーとは後述する G P C 分析により算出される分子量 1 0 0 0 以下の成分である。モノマー量が 0 . 5 重量%を超えると、紡糸・延伸行程で糸切れ等が発生し操業性が著しく低下する。これはモノマー成分が熱により分解する為、ポリ乳酸の耐熱性を低下させるからであると考えられる。

【 0 0 1 5 】

ポリ乳酸中のモノマー量を少なくする為には、重合反応完了間際に反応槽を真空吸引して未反応のモノマーを取り除く、重合チップを適当な液体で洗浄する、固相重合を行うなどの方法を行う。

【 0 0 1 6 】

本発明に用いるポリ乳酸は、その重量平均分子量 M w が好ましくは 1 2 万～2 2 万であり、さらには 1 3 万～1 6 万がより好ましい。また、数平均分子量 M n が好ましくは 6 万～1 1 万、さらには 7 万～9 万がより好ましい。分子量がこの範囲にあると優れた紡糸性、十分な引っ張り強度を得る事ができるが、この範囲外であると紡糸時の分子量低下が大きく、十分な引張強度を得る事ができない。

【 0 0 1 7 】

本発明に用いるポリ乳酸は、その相対粘度 (η_{rel}) が 2 . 7 ～3 . 9 である。この範囲より低いとポリマーの耐熱性が悪くなり、十分な引張強度を得る事ができず、逆に高くなると紡糸温度を上げねばならず、紡糸時の熱劣化が大きい。好ましくは、2 . 9 ～3 . 3 がよい。

【 0 0 1 8 】

マルチフィラメントの相対粘度は、紡糸による低下率が低い程良く、例えばマルチフィラメントの場合、ポリマーに対しての粘度低下率は 7 % 以下であることが好ましい。7 % 以下の場合、紡糸時のポリマーの分解が殆ど無く、紡糸時の糸切れ等の発生もないため紡糸性が良く、延伸工程での引っ張り強度も特に強くな

るからである。

【0019】

本発明では、紡糸速度を3000m/分以上4500m/分以下で紡糸した後、延伸温度を100℃～125℃で、1.3倍以上延伸した後、125℃～150℃で熱セットする事を特徴とする点である。

【0020】

紡糸速度が3000m/分以下では、配向結晶化が不十分で、110℃以上の延伸温度で糸切れが多発し操業性が極めて悪い。又、4500m/分を超えると、糸揺れ、冷却斑等が発生し操業安定性にかける。

【0021】

延伸温度が110℃未満では配向結晶が進まず、糸切れ、延伸斑が発生する。又、125℃を超えると延伸温度が高すぎ延伸時に糸切れが発生する。

【0022】

延伸倍率は1.3倍以上でないと、糸の引張強度が4.5g/d未満と弱く、加工工程で問題が発生する。延伸倍率は1.3倍以上であれば、伸度を調整し、各種加工で使用する事ができる。得られるマルチフィラメントの強伸度のバランス等を考慮すると、延伸倍率は1.3～1.8が好ましく、さらに好ましくは1.5～1.7である。

【0023】

熱セット温度は、125℃未満であればセット温度が低いために、沸水収縮率が高くなり、後加工での収縮が大きく使用できない。150℃を超えると、ポリ乳酸繊維の融点に近づき糸切れが発生する。フィラメントの生産性等を考慮するとセット温度は135～150℃が好ましい。

【0024】

本発明のマルチフィラメントは、引張強度4.5g/d以上が好ましい。引張強度が4.5g/d以上では各種加工で糸切れ等が発生しないので好ましい。又、引張強度が4.5g/d以上になるには複屈折が0.030以上が必要である。

【0025】

マルチフィラメントの熱応力のピーク温度は、常圧染色で染色する場合、染色時のへたりを防ぐために85℃以上である事が好ましく、さらに好ましくは90℃以上必要である。熱応力のピーク温度が85℃以上では染色時のへたりが小さくなるので好ましい。

【0026】

【発明の効果】

本発明の製造方法を用いてポリ乳酸繊維を製造すれば、操業性と繊維物性に優れる生分解性繊維を得る事が出来る。すなわち、耐熱性に優れ熱劣化による紡糸性低下がなく、操業性に優れており、強度、伸度、沸収等の物性値がポリエステル、ナイロン繊維並みの物性を有し、織り・編み等の後工程でも、ポリエステル、ナイロン繊維並みの加工性を得る事ができ、さらに染色時にへたりの少ないポリ乳酸繊維を得る事ができる。

【0027】

【実施例】

以下、実施例により具体的に本発明を説明する。最初に、ポリマー物性の分析方法を紹介する。

【0028】

<分子量><モノマー量>

試料を10mg/mLの濃度になるようクロロホルムに溶かした。クロロホルムを溶媒としてGPC分析を行いMw、Mnを測定した。検出器はRIを用い、分子量の標準物質としてポリスチレンを用いた。

なお、分子量1000以下の成分の割合からポリマー中のモノマー量を算出した。

【0029】

<相対粘度 η_{rel} >

フェノール/テトラクロロエタン=60/40の混合溶媒に試料を1g/dlの濃度になるよう溶解し、20℃でウペローデ粘度管を用いて相対粘度を測定した。

【0030】

< S n 含有量 >

0. 5 g の試料を硫酸／硝酸により湿式灰化した。これを水で希釈して 5 0 m L 溶液とし、I C P 発光分析法により測定した。

【 0 0 3 1 】

(強伸度の測定)

島津製作所製引っ張り試験機を用い、試料長 2 0 c m、速度 2 0 c m / m i n で引っ張り試験を行い破断強度を引っ張り強度、破断伸度を伸度とした。

【 0 0 3 2 】

(沸水収縮率)

初期値 5 0 c m の試料に初期過重 2 0 0 m g をかけて沸騰水中に 1 5 分間浸漬し、5 分間風乾した後、次式により沸水収縮率を求めた。

沸水収縮率 (%) = (初期試料長 - 収縮後の試料長) / 初期試料長 × 1 0 0

【 0 0 3 3 】

(紡糸時粘度低下率)

紡糸ノズルから出てきたマルチフィラメントの相対粘度 (η_{rel}) を測定し、次式により求めた。本実施例における溶融ポリマーの滞留時間は約 1 0 分である。

紡糸時粘度低下率 (%) = { (ポリマー相対粘度 - フィラメントの相対粘度) / ポリマー相対粘度 } × 1 0 0

【 0 0 3 4 】

(複屈折)

繊維の複屈折 Δn は、浸漬液に α -プロモナフタリンを用い、ベレックコンペンセータ法にて測定した。

【 0 0 3 5 】

(熱応力)

カネボウエンジニアリング製熱応力測定装置 TYPE KE-2 S にて測定した。

【 0 0 3 6 】

[ポリマーの重合]

L-ラクチド、D-ラクチドを原料として、オクチル酸スズを重合触媒として、定法によりポリ乳酸を重合した。比較の為に、架橋剤としてトリメリット酸を0.1モル%を加えたものも重合した。得られたポリマーは135℃で固相重合を行い、残存モノマー量の低減を図ったが一部は比較のために固相重合を行わなかった。

【0037】

紡糸操業性は以下のように評価・測定した。

【0038】

(紡糸性評価①)

溶融紡糸により連続7日間の紡糸を行った。紡糸時の糸切れの発生頻度を、以下の3段階(A～C)の基準により評価した。

A ; 糸切れ回数が、0回/7日

B ; 糸切れ回数が、1～2回/7日

C ; 糸切れ回数が、3回以上/7日

【0039】

(紡糸性評価②)

連続7日間の紡糸工程の際に、濾圧上昇等の理由により紡糸口金を交換しなければならなくなった場合、その口金寿命を日数で評価した。

【0040】

(紡糸性評価③)

延伸工程における糸切れの発生頻度を3段階で評価した。(A～C)

A ; 糸切れ回数が0回/7日

B ; 糸切れ回数が1～2回/7日

C ; 糸切れ回数が3回以上/7日

【0041】

(毛羽)

延伸で巻き取った糸の毛羽の発生具合を、以下の2段階の基準(○、×)で評価した。

○ ; 毛羽の発生がない

×；毛羽の発生が見られる。

【0042】

(フィラメント生産性)

紡糸評価①～③と、毛羽の発生具合を勘案して、マルチフィラメントの生産性を以下の3段階の基準(A～C)で総合評価した。

A；大変良好

B；良好

C；不良

【0043】

(染色後へたり)

マルチフィラメントを筒編みサンプルを作成し、分散染料を用いて常圧染色し、染色後サンプルのへたり具合を以下の3段階の基準(A～C)で総合評価した。

A；大変良好(へたり全くなし)

B；良好

C；不良(へたりが大きく商品として使用不可)

【0044】

実施例1～2，比較例1～5

表1はポリマー中のSn含有量を変えたポリマーを紡糸速度3800m/分で紡糸した時の紡糸性①，②と口金寿命の評価結果である。

【0045】

比較例1～3については、Sn含有量(残存触媒量)が特に多いため、紡糸時に解重合が起き、紡糸時の粘度低下率が極めて大きく、紡糸は極めて困難で、口金寿命も1日と短く、実用的には使用できない。

【0046】

比較例4は紡糸時の粘度低下率が17.6%と改良されたが、やはりSn含有量が多いため、口金寿命が3日しかなく、実生産では使用できない。

【0047】

比較例5は、紡糸時の粘度低下率が12.3%と改良されたため、口金寿命は6日に延びたが、やはりSn含有量が35ppmと多いため、7日以上口金寿命

を得る事ができなかった。

【0048】

実施例1, 2はSn含有量が50ppm以下であるために紡糸時の粘度低下率が5.0と少なく紡糸性、口金寿命は極めて良好であった。

【0049】

【表1】

No	実 施 例		比 較 例				
	1	2	1	2	3	4	5
Sn含有量 (ppm)	26	17	824	412	82	62	35
ポリマー 相対粘度 (η_{rel})	2.93	2.98	2.96	2.95	2.97	2.94	3.00
モノマー量 (重量%)	0.26	0.25	0.26	0.23	0.25	0.24	0.26
Mw	12.5×10^4	13.9×10^4	13.9×10^4	13.9×10^4	13.7×10^4	13.5×10^4	14.4×10^4
Mn	6.6×10^4	6.9×10^4	6.8×10^4	6.7×10^4	6.9×10^4	6.6×10^4	7.0×10^4
分岐構造	無し	無し	無し	無し	無し	無し	無し
L体(%)	97.8	96.4	96.4	97.0	96.6	95.5	97.1
紡糸温度 ($^{\circ}\text{C}$)	230	230	230	230	230	230	230
紡糸粘度 低下率(%)	5.0	3.6	73.6	64.3	52.3	17.6	12.3
紡糸速度 (m/分)	3800	3800	3800	3800	3800	3800	3800
紡糸性①	A	A	C	C	C	C~B	B
紡糸性②	≥ 7	≥ 7	1	1	1	3	6

【0050】

実施例 3～5、比較例 6～9 の表 2 はポリマー中のモノマー量を変えて、紡糸速度を 3 5 0 0 m/分 で巻き取った時の紡糸性、口金寿命の結果である。

【 0 0 5 1 】

比較例 6～8 については、ポリマー中のモノマーが特に多いため、紡糸時に熱分解が起きてしまい、紡糸時のポリマー粘度低下率が大きく、紡糸は極めて困難であり、口金寿命も 1 日しかなく、実用的には使用できない。

【 0 0 5 2 】

比較例 9 は、やはりまだモノマー量が多く、口金寿命が 5 日しかないため実生産では使用できない。

【 0 0 5 3 】

実施例 3～5 に付いては、モノマー量を 0. 5 重量% 以下にする事で、紡糸時の熱分解を抑える事ができたため、紡糸時の粘度低下率が 5 % 以下まで改善され、紡糸性、口金寿命、延伸時の毛羽発生具合は極めて良好であった。

【 0 0 5 4 】

【表 2】

	実 施 例			比 較 例			
	3	4	5	6	7	8	9
No							
モノマー量(重量%)	0.46	0.26	0.15	10.2	5.76	3.46	0.98
ポリマー相対粘度 (η rel)	2.97	2.96	2.56	2.96	2.89	2.92	3.02
分岐構造	無し	無し	無し	無し	無し	無し	無し
Sn含有量 (ppm)	19	21	16	18	19	18	17
L体(%)	96.8	98.4	98.4	95.4	96.0	95.6	96.5
Mw	13.8×10^4	14.0×10^4	14.4×10^4	13.9×10^4	13.7×10^4	12.5×10^4	14.4×10^4
Mn	6.8×10^4	6.9×10^4	7.0×10^4	6.7×10^4	6.9×10^4	6.6×10^4	7.0×10^4
紡糸温度(°C)	230	230	230	230	230	230	230
紡糸速度 (m/分)	3500	3500	3500	3500	3500	3500	3500
紡糸粘度低下率 (%)	5	2	1.5	25	20	15	10
紡糸性①	A	A	A	C	C	C	B
紡糸性②	≥ 7	≥ 7	≥ 7	1	1	2	5

【0055】

実施例 6～7、比較例 10～14

表 3、4 は、Sn 含有量を 30 ppm 以下、モノマー量を 0.5% 以下にして、L 体の比率、分岐構造の有り／無し、ポリマーの分子量、相対粘度変化させ、紡糸速度・延伸条件を一定にした時のマルチフィラメントの生産性・マルチフィ

ラメント物性の結果である。

【0056】

実施例 6、比較例 10 は分岐構造の有り／無し以外はほぼ同様の物性を持つポリマーであるが、分岐構造が有る比較例 10 は、紡糸性がやや悪く、延伸時に毛羽の発生が見られ、得られた糸も引っ張り強度が分岐が無いものに比べて弱く、4 g/d 未満で、複屈折 (Δn) も 0.03 以下であり、熱応力のピーク温度が 85℃ 以下であるため、染色時のへたりが大きく実用的には使用できない。

【0057】

また L 体の比率が 95% 未満である表 4 の比較例 14 は、L 体の比率が下がったために紡糸・延伸時に配向結晶が進まず、引っ張り強度が 4 g/d 未満と弱く、沸水収縮率も 30% 以上で、通常の織り・編み加工での寸法安定性が悪くマルチフィラメントとして実用的には使用できない。

【0058】

比較例 11 は、分子量、相対粘度が低いために、紡糸・延伸性が悪くなり、引っ張り強度も 4 g/d 未満と弱くなる。逆に比較例 12、13 は、分子量、相対粘度が高いために紡糸温度を上げなければならず、紡糸温度を上げた事で、紡糸時の粘度低下率が 15% 以上まで大きくなり、紡糸・延伸性は悪く、延伸時に毛羽発生等の問題が発生し実生産には使用できない。

【0059】

【表 3】

No	実 施 例	
	6	7
モノマー量(重量%)	0.27	0.27
ポリマー相対粘度 (η_{rel})	3.02	3.68
分岐構造	無し	無し
Sn含有量(ppm)	18	17
L体(%)	98.7	96.0
Mw	14.6×10^4	19.5×10^4
Mn	7.2×10^4	9.4×10^4
紡糸温度(°C)	230	230
紡糸粘度低下率(%)	3	4
紡糸速度 (m/分)	3500	3500
紡糸性①	A	A
紡糸性②	≥ 7	≥ 7
延伸温度(°C)	110	110
延伸倍率	1.70	1.70
セット温度(°C)	145	145
紡糸性③	A	A
毛羽	○	○
フィラメント生産性	A	A
引張強度(g/d)	5.02	4.96
伸度(%)	30.3	30.8
沸水収縮率(%)	9.8	14.8
複屈折 (Δn)	0.0350	0.0367
ピーク熱応力温度 (°C)	90	91
染色後へたり	A	A

【0 0 6 0】

【表 4】

	比 較 例				
N o	1 0	1 1	1 2	1 3	1 4
モノマー量(重量%)	0.26	0.26	0.25	0.24	0.27
ポリマー相対粘度 (η rel)	3.04	2.58	4.02	4.03	3.02
分岐構造	有り	無し	無し	有り	無し
S n 含有量 (ppm)	19	18	20	18	21
L 体(%)	99.0	96.4	97.0	98.7	92.6
Mw	14.8×10^4	10.2×10^4	23.8×10^4	24.0×10^4	14.5×10^4
Mn	7.6×10^4	5.4×10^4	12.1×10^4	12.4×10^4	7.1×10^4
紡糸温度(℃)	230	230	245	245	230
紡糸粘度低下率 (%)	6	8	15	20	3
紡糸速度 (m/分)	3500	3500	3500	3500	3500
紡糸性①	B	B	C	C	A
紡糸性②	4	4	5	3	≥ 7
延伸温度(℃)	110	110	110	110	110
延伸倍率	1.70	1.70	1.70	1.70	1.70
セット温度(℃)	145	145	145	145	145
紡糸性③	B	C	C	C	B
毛羽	×	×	×	×	×
フィラメント 生産性	C	B	C	C	B
引張強度(g/d)	3.98	3.82	4.02	3.86	3.03
伸度(%)	29.6	28.7	30.2	29.8	30.3
沸水収縮率(%)	10.2	10.1	9.7	10.2	30.5
複屈折 (Δn)	0.0276	0.0265	0.0289	0.0266	0.0235
ピーク熱応力温度 (℃)	82	81	81	82	80
染色後へたり	C	B	B	C	C

【0 0 6 1】

実施例 8～10、比較例 15～19 の表 5、6 は、表 1～4 の結果を基にポリマー物性を、相対粘度 3.09、L 体量 98.2%、モノマー量 0.26wt% で分岐構造を持たないポリ乳酸ポリマーの紡糸・延伸条件を変えた時の紡糸操作性・マルチフィラメント物性の結果である。

【0 0 6 2】

実施例 8 と比較例 15 は同条件で紡糸した糸を、延伸倍率を変えた結果であるが、延伸倍率が 1.3 倍以下である比較例 15 は引張強度、複屈折共に低く、マルチフィラメントとして実用的には使用できない。

【0063】

比較例16は、紡糸速度を2800m/分まで下げた時のテスト結果であるが、2800m/分の巻き取り速度では、配向結晶化が不十分で延伸温度に耐える事ができず、糸切れが多発しマルチフィラメントの生産性が低く実用的には使用できない。

【0064】

実施例9と比較例17は同条件で巻き取った後、延伸温度を変えた時の結果である。延伸温度が低い比較例17は、延伸温度が100℃よりも低いため、延伸温度が不十分であり糸切れ毛羽の発生が見られ、得られた糸も引張強度が弱く、複屈折も低いため実用的には使用できない。

【0065】

実施例9と比較例17は同条件で巻き取った後、セット温度を変えた時の結果である。比較例17ではセット温度が125℃よりも低いため沸水収縮率が20%以上と高く、染色等の後工程での寸法安定性が悪く実用的には使用できない。

【0066】

比較例14は紡糸速度を4500m/分を超える紡速で紡糸した結果である。紡糸速度4800m/分では、紡糸時の糸揺れ、冷却斑が発生し糸切れが多発し操業安定性が悪く、実用的には使用できないが、紡糸速度を4500m/分の実施例10では紡糸・延伸時には全く問題が無く、得られたマルチフィラメントの物性も良好であった。

【0067】

【表 5】

	実 施 例		
N o	8	9	1 0
紡糸温度(℃)	2 3 0	2 3 0	2 3 0
紡糸粘度低下率(%)	3	3	3
紡糸速度 (m/分)	3 2 0 0	4 0 0 0	4 5 0 0
紡糸性①	A	A	A
紡糸性②	≥ 7	≥ 7	≥ 7
延伸温度 (℃)	1 0 5	1 1 5	1 2 0
延伸倍率	1. 7	1. 5	1. 3
セット温度(℃)	1 4 5	1 3 5	1 5 0
紡糸性③	A	A	A
毛羽	○	○	○
フィラメント生産性	A	A	A
引張強度(g/d)	4. 8 9	5. 0 4	5. 1 0
伸度(%)	2 7. 6	2 8. 9	3 0. 0
沸水収縮率(%)	1 0. 2	9. 8	9. 7
複屈折 (Δ n)	0.0332	0.0386	0.0394
ピーク熱応力温度 (℃)	8 7	9 2	9 3
染色後へたり	A	A	A

【0 0 6 8】

【表 6】

	比 較 例				
No	1 5	1 6	1 7	1 8	1 9
紡糸温度(℃)	2 3 0	2 3 0	2 3 0	2 3 0	2 3 0
紡糸粘度低下率 (%)	3	3	3	3	3
紡糸速度 (m/分)	3 2 0 0	2 8 0 0	4 0 0 0	4 0 0 0	4 8 0 0
紡糸性①	○	○	○	○	×
紡糸性②	≥ 7	≥ 7	≥ 7	≥ 7	≥ 7
延伸温度 (℃)	1 0 5	1 0 5	9 0	1 0 5	1 2 0
延伸倍率	1. 2	1. 9	1. 5	1. 5	1. 3
セット温度(℃)	1 5 0	1 5 0	1 5 0	1 1 5	1 5 0
紡糸性③	C	C	B	A	C
毛羽	×	×	×	○	×
フィラメント 生産性	C	C	B	B	C
引張強度(g/d)	3. 2 1	4. 1 2	3. 9 6	4. 8 7	4. 7 4
伸度(%)	3 5. 0	2 7. 6	2 7. 4	2 8. 6	2 5. 4
沸水収縮率(%)	1 5. 0	1 1. 7	1 0. 5	2 0. 7	9. 8
複屈折 (Δ n)	0.0251	0.0271	0.0281	0.0310	0.0364
ピーク熱応力温度 (℃)	7 8	8 1	7 9	8 3	9 0
染色後へたり	C	B	B	C	B

【書類名】 要約書

【要約】

【課題】 操業性に優れ、繊維物性に優れるポリ乳酸繊維とその製造方法を提供する。

【解決手段】 L体が95%以上であり、相対粘度が2.7～3.9であり、モノマー量が0.5重量%以下であり、Snの含有量が30ppm以下であり、直鎖状であるポリ乳酸樹脂を使用して、3000m/分以上4500m/分以下で紡糸した後、延伸温度100℃～125℃で、1.3倍以上延伸した後、125℃～150℃で熱セットし、得られたフィラメントの引張強度4.5g/d以上、沸水収縮率が12%以下で、複屈折が0.030以上、熱応力測定値のピーク温度が85℃以上の物性を持つポリ乳酸マルチフィラメントの製造方法。

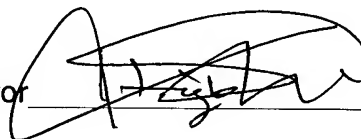
【選択図】 なし

VERIFICATION OF TRANSLATION

I, Ikuo HIGASHI, of 8-10, Toranomom 2-chome, Minato-ku, Tokyo, Japan, am the translator of the documents attached and I state that the following is a true translation to the best of my knowledge and belief of Japanese Patent Application No. 11-205836.

Dated this on April 30, 2002

Signature of translator

A handwritten signature in black ink, appearing to be 'Ikuo Higashi', written over a horizontal line.

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[Title of the Invention] MULTIFILAMENT AND PROCESS FOR PRODUCING THEREOF

[Claims]

[Claim 1] A multifilament characterized by comprising a polylactic acid resin wherein the polylactic acid resin comprises 98% or more of L-isomer and has a relative viscosity of 2.7 to 3.9, the monomer content is 0.5% by weight or less, the Sn (tin) content is 30 ppm or less and the polylactic acid resin is in a linear.

[Claim 2] A multifilament characterized in that the multifilament comprises 98% or more of L-isomer, the monomer content is 0.5% by weight or less, the Sn (tin) content is 30 ppm or less, the multifilament is in a linear, and the molecular weight is 120,000 to 220,000 in terms of a weight average molecular weight Mw and 60,000 to 110,000 in terms of a number average molecular weight Mn.

[Claim 3] The multifilament according to claim 1 or 2, wherein the tensile strength is 4.5 g/d or more, the contraction ratio in boiling water is 12% or less, the birefringence is 0.030 or more, and the peak temperature of thermal stress is 85°C or more.

[Claim 4] A process for producing a polylactic acid multifilament characterized in that the production of the polylactic acid multifilament uses the polylactic acid according to claim 1 or 2, and comprises spinning at a rate of not less than 3,000 m/min and not more than 4,500 m/min, then drawing at a drawing temperature of 100°C to 125°C into 1.3 times or more,

and thereafter heat-setting at a temperature of 125°C to 150°C.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Pertains]

The present invention relates to a synthetic fiber having biodegradability and to a process for producing the fiber.

[0002]

[Prior Art]

The multifilament fiber material that is now used most widely is the synthetic resin such as polyesters represented by polyethylene terephthalate and polyamides represented by nylon 6 and nylon 66.

[0003]

Although the synthetic resin has the merit that it can be produced in large quantities at low cost, there is a problem with it concerning a method of its disposal after use. That is, a fiber formed of a synthetic resin mentioned above hardly decomposes in the natural environment and it has a possibility of generating a great amount of heat of combustion on its destruction by fire.

[0004]

Then, there recently have been proposals of using polycaprolactone, polylactic acid and so on, which are synthetic resins having biodegradability, for fiber applications. These synthetic resins certainly have the merit of having biodegradability, but there are more problems with them concerning practicality in comparison with the conventional

(non-biodegradable) synthetic resins.

[0005]

Conventionally, in the polylactic acid-type biodegradable fiber, a method is adopted in which a fiber is produced by a conventional method comprising spinning at a low speed of 3,000 m/min or less and then performing a drawing process. For example, in JP-A-7-216646 and JP-A-7-133569, a method in which an undrawn polylactic acid fiber extruded at a speed of 1,000 m/min or less is wound up and an oriented fiber is obtained in a drawing process is proposed, but it is necessary to copolymerize polyethylene glycol.

[0006]

However, even by these approaches, it is difficult to improve the workability in the production process and it is not possible to obtain fibers having physical properties and workability equivalent to fibers obtained using a conventional (non-biodegradable) synthetic resin as a raw material.

[0007]

[Problem to be Solved by the Invention]

The inventors of the present invention provide a process for producing a polylactic acid multifilament which has physical property values about strength, elongation, contraction ratio in boiling water and so on comparable to polyesters and nylon fibers and also exhibits processability comparable to polyesters and nylon fibers even in post-processes such as weaving, knitting and dyeing, by severely examining the physical properties of a polylactic acid used as a raw material of fiber, using a polylactic

acid having specific physical properties and examining the spinning and drawing process.

[0008]

[Means for Solving the Problem]

The above-mentioned object can be attained with a multifilament characterized by comprising a polylactic acid resin wherein the polylactic acid resin comprises 98% or more of L-isomer and has a relative viscosity of 2.7 to 3.9, the monomer content is 0.5% by weight or less, the Sn (tin) content is 30 ppm or less and the polylactic acid resin is in a linear.

[0009]

[Mode for Carrying out the Invention]

The polylactic acid used for the present invention has a linear structure. In other words, it has almost no branched structure. In the conventional proposals, in order to improve the melt viscosity and the degree of polymerization, a little amount of branching agent is added when a polylactic acid is polymerized. However, the inventors of the present invention confirmed that in the production of a polylactic acid fiber, the branched structure of the raw material resin acts on the spinning workability far negatively in comparison to the usual polyester fibers. In other words, a polylactic acid having a branched structure, even if in a very slight amount, has a problem of tensile strength weaker than that a polylactic acid having no branched structure has.

[0010]

In order to eliminate a branched structure, it is

recommended never to use anything that causes the raw material of a polymer to generate a branched structure, or any trivalent or tetravalent alcohol, or any carboxylic acid. Even in the case of using a component having such a structure from another certain reason, it is important to limit the amount of such a component to a minimum amount such that spinning operations such as yarn breakage are not affected.

[0011]

The polylactic acid used for the present invention is obtained by using L-lactic acid, D-lactic acid, or L-lactide or D-lactide which are dimers of lactic acid as a raw material, and it is important that the polylactic acid is one comprising 98% or more of L-isomer. This is because when the proportion of D-isomer is increased, a polylactic acid becomes to have a non-crystalline structure and oriented crystallization does not proceed during a spinning and drawing process, resulting in poor physical properties of fibers to be obtained. In particular, the tensile strength is greatly reduced while the contraction ratio in boiling water becomes too great, and therefore, such a polylactic acid cannot be practically used.

[0012]

In the polylactic acid used for the present invention, the Sn content in the polymer must be 30 ppm or less, and is preferably 20 ppm or less. An Sn-based catalyst is used as a polymerization catalyst of polylactic acids. However, if it exists in a content exceeding 30 ppm, depolymerization occurs during spinning and therefore the nozzle filtering pressure increases in a short

period of time, resulting in a remarkable deterioration of spinning workability.

[0013]

The amount of Sn can be reduced by saving in the amount thereof used in polymerization or by washing chips with a suitable liquid.

[0014]

In the polylactic acid used for the present invention, the monomer content is 0.5% by weight or less, preferably 0.3% by weight or less, and especially preferably 0.2% by weight or less. By the "monomer" referred to in the present invention is meant components having molecular weights not more than 1,000 determined by the GPC analysis described later. If the monomer content exceeds 0.5% by weight, yarn breakage or the like occurs during the spinning and drawing process, resulting in a remarkable deterioration of workability. This is probably because decomposition of monomer components caused by heat leads to deterioration of a polylactic acid.

[0015]

In order to lessen the monomer content in a polylactic acid, methods are carried out such as removing unreacted monomers by vacuum suction of a reaction vessel just before the completion of a polymerization reaction, washing polymerization chips with a suitable liquid, and performing a solid-state polymerization.

[0016]

The polylactic acid used for the present invention preferably has a weight average molecular weight Mw of 120,000

to 220,000, more preferably 130,000 to 160,000. Its number average molecular weight M_n is preferably 60,000 to 110,000, more preferably 70,000 to 90,000. When the molecular weight is within these ranges, a good spinning property and a sufficient tensile strength can be obtained. If it is out of these ranges, a great reduction in molecular weight is caused during spinning and no sufficient tensile strength can be obtained.

[0017]

The polylactic acid used for the present invention has a relative viscosity (η_{rel}) of 2.7 to 3.9. If it is lower than this range, a polymer becomes poor in heat resistance and no sufficient tensile strength can be obtained. In contrast, if it becomes high, the spinning temperature must be raised and a great thermal degradation is caused during spinning. The relative viscosity is preferably 2.9 to 3.3.

[0018]

As for the relative viscosity of a multifilament, the lower the coefficient of its reduction caused by spinning, the better. For example, in the case of multifilament, the coefficient of viscosity reduction with respect to a polymer is preferably 7% or less. This is because when it is 7% or less, almost no decomposition of polymers occurs during spinning and no troubles such as yarn breakage occur during spinning, so that the spinning property is good, and the tensile strength in the drawing process becomes particularly great.

[0019]

The present invention is characterized by spinning at a

spinning speed of not less than 3,000 m/min and not more than 4,500 m/min, then drawing at a drawing temperature of 100°C to 125°C into 1.3 times or more, and then heat-setting at 125°C to 150°C.

[0020]

A spinning speed of 3,000 m/min or less results in insufficient oriented crystallization, which leads to frequent occurrence of yarn breakage at spinning temperatures 110°C or higher and, therefore, to a very bad workability. A spinning speed exceeding 4,500 m/min causes swing of yarn, uneven cooling and so on, and therefore, results in poor operation stability.

[0021]

If the drawing temperature is lower than 110°C, oriented crystallization does not proceed, resulting in yarn breakage and uneven drawing. On the other hand, if the drawing temperature exceeds 125°C, such a drawing temperature is too high and yarn breakage occurs during drawing.

[0022]

Unless the draw magnification factor is 1.3 times or more, the tensile strength of yarn is as weak as less than 4.5 g/d, and problems will occur during processing steps. If the draw magnification factor is 1.3 times or more, it is possible to adjust the elongation and the product can be used for various kinds of processing. Considering the balance of tensile strength, elongation and so on of the multifilament to be obtained, the draw magnification factor is preferably 1.3 to 1.8, more preferably 1.5 to 1.7.

[0023]

If the heat-setting temperature is lower than 125°C, the contraction ratio in boiling water becomes high due to such a low setting temperature. The resultant yarn exhibits so great shrinkage in a post-processing that it cannot be used. If the heat-setting temperature exceeds 150°C, the temperature of a polylactic acid fiber processed becomes close to its melting point and yarn breakage occurs. Considering productivity of filaments and so on, the setting temperature is preferably 135 to 150°C.

[0024]

The multifilament of the present invention preferably has a tensile strength of 4.5 g/d or more. Tensile strength of 4.5 g/d or more are desirable since yarn breakage or the like does not occur during various kinds of processing. In order for a tensile strength to become 4.5 g/d or more, the birefringence must be 0.030 or more.

[0025]

In order to prevent a multifilament from wear-out during dyeing by the normal pressure dyeing, the peak temperature of thermal stress of a multifilament is preferably 85°C or higher, more preferably 90°C or higher. The peak temperatures of thermal stress of 85°C or higher are desirable because less wear-out is caused during dyeing.

[0026]

[Effect of the Invention]

If a polylactic acid fiber is produced using the process

for producing of the present invention, a biodegradable fiber excellent in workability and in fiber physical properties can be obtained. In other words, a polylactic acid fiber can be obtained, the fiber being excellent in heat resistance, exhibiting no reduction in spinning property caused by thermal degradation, being excellent in workability, having physical property values about strength, elongation, contraction ratio in boiling water and so on comparable to polyesters and nylon fibers, exhibiting processability comparable to polyesters and nylon fibers even in post-processes such as weaving, knitting and dyeing, and generating less wear-out during dyeing.

[0027]

[Example]

Hereafter, the present invention will be explained concretely with reference to Examples. First, methods for analyzing physical properties of polymers are introduced.

[0028]

<Molecular weight> <Monomer content>

A sample was dissolved in chloroform so that the concentration might become 10 mg/mL. Mw and Mn were measured by GPC analysis using chloroform as a solvent. RI was used as a detector. Polystyrene was used as a reference material.

In addition, the monomer content in a polymer was calculated from the ratio of the components having molecular weights of 1,000 or less.

[0029]

<Relative viscosity η_{rel} >

The relative viscosity was measured with an Ubbelohde's viscosity tube at 20°C after dissolving a sample in a mixed solvent of phenol/tetrachloroethane = 60/40 so that the concentration of the sample might become 1 g/dL.

[0030]

<Sn content>

0.5 g of sample was subjected to wet-ashing with sulfuric acid/nitric acid. The resultant was diluted with water into a 50 mL solution. Thereafter, the Sn content was measured by ICP emission spectrophotometry.

[0031]

(Measurement of tensile strength and elongation)

Using a tensile tester manufactured by Shimadzu Corporation, a tensile test was performed under the following conditions, a sample length of 20 cm and a tensile speed of 20 cm/min. The strength at breakage and the elongation at breakage were, respectively, taken as the tensile strength and the elongation.

[0032]

(Contraction ratio in boiling water)

After application of an initial load of 200 g to a sample having an initial length of 50 cm, followed by immersion of the sample in a boiling water for 15 minutes, followed by drying it in the air for 5 minutes, the contraction ratio in boiling water was calculated according to the following formula.

Contraction ratio in boiling water (%) = (Initial sample

$$\frac{\text{length} - \text{Sample length after shrinkage}}{\text{Initial sample length}} \times 100$$

[0033]

(Reduction coefficient of viscosity during spinning)

The relative viscosity (η_{rel}) of a multifilament came out of a spinning nozzle was measured and the reduction coefficient of viscosity during spinning was calculated according to the following formula. The residence time of the molten polymer in this Example was about 10 minutes.

$$\text{Reduction coefficient of viscosity during spinning (\%)} = \frac{(\text{Relative viscosity of a polymer} - \text{Relative viscosity of filaments})}{(\text{Relative viscosity of polymer})} \times 100$$

[0034]

(Birefringence)

Birefringence Δn of a fiber was measured by the Berek compensator method using α -bromonaphthalene as an immersion liquid.

[0035]

(Thermal stress)

Thermal stress was measured with a thermal stress measuring apparatus TYPE KE-2S manufactured by Kanebo ENGINEERING, LTD.

[0036]

[Polymerization of a polymer]

A polylactic acid was polymerized by the usual method using L-lactide and D-lactide as raw materials and tin octylate as a polymerization catalyst. For comparison, a polymer containing 0.1 mol% of trimellitic acid as a cross linking agent was also

polymerized. The polymers obtained were subjected to solid-state polymerization at 135°C to reduce the amount of residual monomers. However, for comparison, the polymers were partially left without being subjected to the solid-state polymerization.

[0037]

The spinning workability was evaluated and measured as follows.

[0038]

(Evaluation of spinning ability 1)

Continuous seven-day spinning was carried out by melt spinning. The frequency of yarn breakage during the spinning was evaluated according to the following three-level (A to C) standard.

A; The frequency of yarn breakage is 0 time / 7 days.

B; The frequency of yarn breakage is 1 to 2 times / 7 days.

C; The frequency of yarn breakage is 3 times or more / 7 days.

[0039]

(Evaluation of spinning ability 2)

In the case where a spinneret became to have to be changed due to increase of filtering pressure or the like in the continuous seven-day spinning, the life of the spinneret was evaluated in terms of the number of days.

[0040]

(Evaluation of spinning ability 3)

The frequency of yarn breakage in a drawing process was evaluated on a three-level scale (A to C).

A; The frequency of yarn breakage is 0 time / 7 days.

B; The frequency of yarn breakage is 1 to 2 times / 7 days.

C; The frequency of yarn breakage is 3 times or more / 7 days.

[0041]

(Fluff)

The condition of fluff formation in a yarn wound-up during drawing was rated based on the following two-level standard (, x).

: No formation of fluff is found.

x: Formation of fluff is found.

[0042]

(Productivity of filament)

Taking spinning evaluations 1 to 3 and the condition of fluff formation into account, the productivity of a multifilament was evaluated synthetically according to the following three-level standard (A to C).

A; Very good

B; Good

C; Poor

[0043]

(Wear-out after dyeing)

A cylindrically knitted sample was prepared from a filament. The sample was dyed under normal pressure with a disperse dye. The wear-out of the sample after dyeing was evaluated synthetically according to the following three-level standard (A to C).

A; Very good (There was no wear-out.)

B; Good

C; Poor (There was so great wear-out that the multifilament cannot be used as a product for sale.)

[0044]

Examples 1 to 2, Comparative Examples 1 to 5

Table 1 provides the evaluation results about the spinning abilities 1, 2 and the life of a spinneret determined in the spinning of polymers with different Sn contents in the polymers at a spinning speed of 3,800 m/min.

[0045]

Comparative Examples 1 to 3 cannot be used practically because depolymerization occurred during spinning due to a particularly great Sn content (the amount of residual catalyst), resulting in a great reduction coefficient of viscosity during the spinning and it was very difficult to perform spinning and the life of a spinneret was as short as one day.

[0046]

In Comparative Example 4, the reduction coefficient of viscosity during spinning was improved to 17.6%, but since Sn content was still high, the life of a spinneret was only three days. Therefore, such Comparative Example cannot be used in practical production.

[0047]

In Comparative Example 5, since the reduction coefficient of viscosity during spinning was improved to 12.3%, the life of a spinneret was extended to six days. However, it was not possible to achieve a life of spinneret of seven days or more because of the great Sn content as much as 35 ppm.

[0048]

In Examples 1 and 2, since the Sn content was not greater than 50 ppm, the reduction coefficient of viscosity during spinning was as low as 5.0, and the spinning ability and the life of a spinneret were very good.

[0049]

[Table 1]

No	Example		Comparative Example				
	1	2	1	2	3	4	5
Sn content (ppm)	26	17	824	412	82	62	35
Relative viscosity of polymer (η_{rel})	2.93	2.98	2.96	2.95	2.97	2.94	3.00
Monomer content (% by weight)	0.26	0.25	0.26	0.23	0.25	0.24	0.26
Mw	12.5×10^4	13.9×10^4	13.9×10^4	13.9×10^4	13.7×10^4	13.5×10^4	14.4×10^4
Mn	6.6×10^4	6.9×10^4	6.8×10^4	6.7×10^4	6.9×10^4	6.6×10^4	7.0×10^4
Branched structure	None	None	None	None	None	None	None
L-isomer (%)	97.8	96.4	96.4	97.0	96.6	95.5	97.1
Spinning temperature (°C)	230	230	230	230	230	230	230
Rate of decrease of viscosity during spinning (%)	5.0	3.6	73.6	64.3	52.3	17.6	12.3
Spinning speed (m/min)	3,800	3,800	3,800	3,800	3,800	3,800	3,800
Spinning ability - 1	A	A	C	C	C	C-B	B
Spinning ability - 2	≥ 7	≥ 7	1	1	1	3	6

[0050]

Table 2 about Examples 3 to 5 and Comparative Examples 6 to 9 provides the results concerning the spinning abilities and the life of a spinneret determined when the monomer content in polymers was varied and winding-up was carried out at a spinning speed of 3,500 m/min.

[0051]

Comparative Examples 6 to 8 cannot be used practically because thermal decomposition occurred during spinning due to the particularly great amounts of monomers in the polymers, resulting in great reduction coefficients of viscosity during the spinning and it was very difficult to perform spinning and the life of a spinneret was as short as one day.

[0052]

Comparative Example 9 cannot be used in practical production since the monomer content was still great and the life of a spinneret was only five days.

[0053]

As for Examples 3 to 5, by setting the monomer content to 0.5% by weight or less, heat decomposition during spinning can be controlled and the reduction coefficient of viscosity, therefore, was improved to 5% or less. The spinning ability, the life of a spinneret and the condition of fluff formation during drawing were extremely good.

[0054]

[Table 2]

	Example			Comparative Example			
No	3	4	5	6	7	8	9
Monomer content (% by weight)	0.46	0.26	0.15	10.2	5.76	3.46	0.98
Relative viscosity of polymer (η_{rel})	2.97	2.96	2.56	2.96	2.89	2.92	3.02
Branched structure	None	None	None	None	None	None	None
Sn content (ppm)	19	21	16	18	19	18	17
L-isomer (%)	96.8	98.4	98.4	95.4	96.0	95.6	96.5
Mw	13.8×10^4	14.0×10^4	14.4×10^4	13.9×10^4	13.7×10^4	12.5×10^4	14.4×10^4
Mn	6.8×10^4	6.9×10^4	7.0×10^4	6.7×10^4	6.9×10^4	6.6×10^4	7.0×10^4
Spinning temperature ($^{\circ}\text{C}$)	230	230	230	230	230	230	230
Spinning speed (m/min)	3,500	3,500	3,500	3,500	3,500	3,500	3,500
Rate of decrease of viscosity during spinning (%)	5	2	1.5	25	20	15	10
Spinning ability - 1	A	A	A	C	C	C	B
Spinning ability - 2	≥ 7	≥ 7	≥ 7	1	1	2	5

[0055]

Examples 6 to 7, Comparative Examples 10 to 14

Tables 3 and 4 provides the results about the productivity of a multifilament and physical properties of the multifilament, the results being obtained when the Sn content and the monomer content were set to 30 ppm or less and 0.5% or less, respectively, and the percentage of L-isomer, whether a branched structure was present or not, the molecular weight and the relative viscosity of the polymers were varied, and the spinning speed and the drawing conditions were kept constant.

[0056]

Example 6 and Comparative Example 10 concern polymers

having almost the same physical properties except whether a branched structure was present or not. However, in Comparative Example 10 with a branched structure, the spinning ability was a little poor and the formation of fluff was found during drawing. The resultant yarn had a tensile strength less than 4 g/d, which was weaker than the polymer with no branch. The birefringence (Δn) was 0.03 or less and the peak temperature of thermal stress was not higher than 85°C. Therefore, the wear-out in dyeing was great and this Comparative Example cannot be used practically.

[0057]

In Comparative Example 14 given in Table 4, in which the percentage of L-isomer was less than 95%, since the percentage of L-isomer was dropped, oriented crystallization did not proceed during the spinning and drawing. The tensile strength was as weak as less than 4 g/d and the contraction ratio in boiling water was 30% or more. The dimensional stability in the usual weaving and knitting processing was poor. Therefore, the product cannot be used practically as a multifilament.

[0058]

In Comparative Example 11, the spinning and drawing properties became poor and the tensile strength also became as weak as less than 4 g/d because of the low molecular weight and relative viscosity. Conversely, in Comparative Examples 12 and 13, there was a necessity of raising the spinning temperature because of the high molecular weight and relative viscosity. The raising of the spinning temperature rendered the reduction coefficient of viscosity during the spinning not less than 15%,

resulting in poor spinning and drawing properties. During the drawing, there occurred problems of fluff formation and so on, thus, these Comparative Examples cannot be used for practical production.

[0059]

[Table 3]

No	Example	
	6	7
Monomer content (% by weight)	0.27	0.27
Relative viscosity of polymer (η_{rel})	3.02	3.68
Branched structure	None	None
Sn content (ppm)	18	17
L-isomer (%)	98.7	96.0
Mw	14.6×10^4	19.5×10^4
Mn	7.2×10^4	9.4×10^4
Spinning temperature (°C)	230	230
Rate of decrease of viscosity during spinning (%)	3	4
Spinning speed (m/min)	3,500	3,500
Spinning ability - 1	A	A
Spinning ability - 2	≥ 7	≥ 7
Draw temperature (°C)	110	110
Draw magnification factor	1.70	1.70
Set temperature (°C)	145	145
Spinning ability - 3	A	A
Fluffs		
Productivity of filament	A	A
Tensile strength (g/d)	5.02	4096
Elongation (%)	30.3	30.8
Contraction rate in boiling water (%)	9.8	14.8
Birefringence (Δn)	0.0350	0.0367
Thermal stress peak temperature (°C)	90	91
wear-out after dying	A	A

[0060]

[Table 4]

[Table 4]

	Comparative Example				
No	10	11	12	13	14
Monomer content (% by weight)	0.26	0.26	0.25	0.24	0.27
Relative viscosity of polymer (η_{rel})	3.04	2.58	4.02	4.03	3.02
Branched structure	Yes	None	None	Yes	None
Sn content (ppm)	19	18	20	18	21
L-isomer (%)	99.0	96.4	97.0	98.7	92.6
Mw	14.8×10^4	10.2×10^4	23.8×10^4	24.0×10^4	14.5×10^4
Mn	7.6×10^4	5.4×10^4	12.1×10^4	12.4×10^4	7.1×10^4
Spinning temperature ($^{\circ}\text{C}$)	230	230	245	245	230
Rate of decrease of viscosity during spinning (%)	6	8	15	20	3
Spinning speed (m/min)	3,500	3,500	3,500	3,500	3,500
Spinning ability - 1	B	B	C	C	A
Spinning ability - 2	4	4	5	3	≥ 7
Draw temperature ($^{\circ}\text{C}$)	110	110	110	110	110
Draw magnification factor	1.70	1.70	1.70	1.70	1.70
Set temperature ($^{\circ}\text{C}$)	145	145	145	145	145
Spinning ability - 3	B	C	C	C	B
Fluffs	x	x	x	x	x
Productivity of filament	C	B	C	C	B
Tensile strength (g/d)	3.98	3.82	4.02	3.86	3.03
Elongation (%)	29.6	28.7	30.2	29.8	30.3
Contraction rate in boiling water (%)	10.2	10.1	9.7	10.2	30.5
Birefringence (Δn)	0.0276	0.0265	0.0289	0.0266	0.0235
Thermal stress peak temperature ($^{\circ}\text{C}$)	82	81	81	82	80
wear-out after dyeing	C	B	B	C	C

[0061]

Tables 5 and 6 about Examples 8 to 10 and Comparative Examples 15 to 19 provide the results concerning the spinning workability and the physical properties of multifilaments obtained by changing the polymer physical properties to a relative viscosity of 3.09, an L-isomer amount of 98.2%, and a monomer content of 0.26 wt% and changing the spinning and drawing conditions of the polylactic acid polymer with no branched structure.

[0062]

Example 8 and Comparative Example 15 are the results obtained by changing the draw magnification factor of yarns spun under the same conditions. In Comparative Example 15 where the draw magnification factor was not greater than 1.3 times, both the tensile strength and the birefringence were low and the product cannot be used practically as a multifilament.

[0063]

Comparative Example 16 provides the test results obtained when the spinning speed was reduced to 2,800 m/min. At a winding-up speed of 2,800 m/min, oriented crystallization was insufficient and the material was not proof against the drawing temperature and therefore yarn breakage occurred frequently. Therefore, the productivity of a multifilament was so low that the Comparative Example cannot be used practically.

[0064]

Example 9 and Comparative Example 17 provide the results obtained by varying the drawing temperature after winding-up under the same conditions. In Comparative Example 17 where the

drawing temperature was low, since the drawing temperature was lower than 100°C, the drawing temperature was insufficient, and yarn breakage and fluff formation were observed. The yarn obtained had a poor tensile strength and low birefringence. Therefore, this Comparative Example cannot be used practically.

[0065]

Example 9 and Comparative Example 17 provide the results obtained when the setting temperature was changed after winding up under the same conditions. In Comparative Example 17, since the setting temperature was lower than 125°C, the contraction ratio in boiling water was as high as 20% or more, and the dimensional stability after the post processing such as dyeing was poor. Thus, this Comparative Example cannot be use practically.

[0066]

Comparative Example 14 is the result obtained by carrying out the spinning at a spinning speed exceeding 4,500 m/min. At a spinning speed of 4,800 m/min, there occurred swing of yarn and uneven cooling during the spinning and yarn breakage occurred frequently, resulting in poor operation stability. Therefore, this Comparative Example cannot be used practically. However, in Example 10 where the spinning speed was 4,500 m/min, there arose no problem during the spinning and drawing and the multifilament obtained had good physical properties.

[0067]

[Table 5]

No	Example		
	8	9	10
Spinning temperature (°C)	230	230	230
Rate of decrease of viscosity during spinning (%)	3	3	3
Spinning speed (m/min)	3,200	4,000	4,500
Spinning ability - 1	A	A	A
Spinning ability - 2	≥7	≥7	≥7
Draw temperature (°C)	105	115	120
Draw magnification factor	1.7	1.5	1.3
Set temperature (°C)	145	135	150
Spinning ability - 3	A	A	A
Fluffs			
Productivity of filament	A	A	A
Tensile strength (g/d)	4.89	5.04	5.10
Elongation (%)	27.6	28.9	30.0
Contraction rate in boiling water (%)	10.2	9.8	9.7
Birefringence (Δn)	0.0332	0.0386	0.0394
Thermal stress peak temperature (°C)	87	92	93
wear-out after dying	A	A	A

[0068]

[Table 6]

No	Comparative Example				
	15	16	17	18	19
Spinning temperature (°C)	230	230	230	230	230
Rate of decrease of viscosity during spinning (%)	3	3	3	3	3
Spinning speed (m/min)	3,200	2,800	4,000	4,000	4,800
Spinning ability - 1					×
Spinning ability - 2	≥7	≥7	≥7	≥7	≥7
Draw temperature (°C)	105	105	90	105	120
Draw magnification factor	1.2	1.9	1.5	1.5	1.3
Set temperature (°C)	150	150	150	115	150
Spinning ability - 3	C	C	B	A	C
Fluffs	×	×	×		×
Productivity of filament	C	C	B	B	C
Tensile strength (g/d)	3.21	4.12	3.96	4.87	4.74
Elongation (%)	35.0	27.6	27.4	28.6	25.4
Contraction rate in boiling water (%)	15.0	11.7	10.5	20.7	9.8
Birefringence (Δn)	0.0251	0.0271	0.0281	0.0310	0.0364
Thermal stress peak temperature (°C)	78	81	79	83	90
wear-out after dying	C	B	B	C	B

[Title of Document] Abstract

[Abstract]

[Problem]

To provide a polylactic acid fiber that is excellent in workability and also in fiber physical properties, and a process for producing thereof.

[Solving Means]

A process for producing a polylactic acid multifilament using a polylactic acid resin wherein the polylactic acid comprises 98% or more of L-isomer and has a relative viscosity of 2.7 to 3.9, the monomer content is 0.5% by weight or less, the Sn (tin) content is 30 ppm or less and the polylactic acid is in a linear, the method comprising spinning at a rate of not less than 3,000 m/min and not more than 4,500 m/min, then drawing at a drawing temperature of 100°C to 125°C into 1.3 times or more, and thereafter heat-setting at a temperature of 125°C to 150°C, the obtained filament having physical properties: a tensile strength of 4.5 g/d or more, a contraction ratio in boiling water of 12% or less, a birefringence of 0.030 or more, and a peak temperature of the thermal stress measurements of 85°C or higher.

[Selection drawing] None